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Chemical Changes in Milk Powder During Manufacture and Storage and Response of the Taste Mechanism to these Changes

SUMMARY

Attempts are being made to isolate and identify the flavor substances produced during the heating and storage of milk products. The evidence to date suggests that the caramelized principle (or principles) is an ether soluble weakly acidic substance which remains liquid at -23° C. The presence of tightly-bound reduced sulfur had been demonstrated in this fraction which might account for the disappearance of sulfhydryl compounds as the caramelized flavor develops. Further work is being done to isolate pure forms of the flavor compounds or crystalline derivatives with the purpose of characterization in mind.

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CHEMICAL CHANGES IN MILK POWDER DURING MANUFACTURE AND STORAGE AND RESPONSE OF THE TASTE MECHANISM TO THESE CHANGES

At the present time, attempts are being made to isolate compounds responsible for the so-called "caramelized flavor" of heated dairy products. This flavor appears to manifest itself in all dairy products which have been subjected to rigorous heat treatment. The aging of such products, particularly at elevated temperatures, intensifies the "caramelized flavor" and other flavors which have their origin in the storage process. In particular, dried milk, as well as evaporated milk, suffers from these deteriorative flavor changes resulting from heating, concentrating and storage.

The first clue as to the nature and means of isolation of the "caramelized flavor" was made evident in the observations that the "caramelized" principle will dialyze from a sample of heated milk through a cellophane membrane. This enabled separation of the flavor from the protein fraction of the milk. The diffusate, in this case, is a yellowish-green color, similar to that of unheated milk. Extraction of the diffusate with ether and evaporation of the ether extract to remove all of the ether accomplishes a high degree of concentration of the "caramelized flavor" principle. That such is the case was verified by the qualitative odor descriptions of the extract residue by many impartial observers. In order to maintain purity of the flavor principle under these conditions, it is necessary to use freshly redistilled ether. In these experiments, only the ether fraction distilling between 34.5 and 35.5°C was used.

In an attempt to eliminate the dialyzing process, it was observed that ether extraction of heated concentrated milks resulted in the formation of emulsions which are very difficult to break but that heated skimmilk lends itself well to direct extraction with very little emulsification of the ether. Since butter fat appears to be of little importance in the "caramelized flavor" mechanism, it was decided to continue the experiments using heated skimmilk. It must be borne in mind that any technique which will isolate the flavor principle in a greater state of purity and in greater quantity is highly desirable. The present indications are that many gallons of heated skimmilk will have to be processed in order to isolate one or two grams of the principle flavor compound involved.

A preliminary study of the chemical nature of the caramelized flavor residue and of the physical characteristics of the flavor has revealed the following:

1. That reduced sulfur is present as indicated both by sodium fusion and alkaline hydrolysis (acidification of the hydrolysate liberates H_2S.)

2. Tests for nitrogen have been negative thus far although its presence has not been ruled out in as much as the quantities present and the sensitivity of the tests used may be in question.

3. The flavor is not distillable from the residue at atmospheric pressure.

4. Although the flavor residue is yellow when freshly isolated, it turns brown quite rapidly. This change is augmented by heating, drying and alkalinity.

5. The residue is acid to litmus and the solubility characteristics of the flavor, judging by odor and extractability from one solvent to another is roughly as follows:

HCL	Least soluble
Water	↑
Petroleum ether	
Ethyl ether	
Na_2CO_3	↓
NaOH	Most soluble

6. The dry flavor residue free of fat, fatty acids, and ether is liquid to a temperature of -23°C.

7. When a water solution of the flavor residue is titrated with NaOH to the phenolphthalein end point it is possible to extract the flavor with ether. This would indicate that the flavor is not a strong acid for two reasons. First, sodium salts are not generally soluble in ether, and second, sodium salts ordinarily do not have much odor. However, the flavor compound cannot be extracted from sodium hydroxide solution with ether, but when the NaOH solution is neutralized with HCL it is again possible to extract the flavor with ether.

Thus, for the moment, it is being assumed that the flavor compound (or compounds) is a weak acid. Present attempts are being made to prepare the flavor in pure form or a derivative thereof. The formation of a sodium salt which might be precipitated from alkaline solution with acetone offers definite possibilities for preparing a pure crystalline derivative. In this way it would be possible to regenerate the flavor from the derivative by acidification. The background chemistry as to how this end-product may be formed and what ingredients of milk are requisite to its formation are also being studied and experimentally investigated. There is evidence that phosphates are important in the caramelized flavor mechanism just as they are in carbohydrate dissimilation by fermentation organisms; stages of the destruction of lactose may require activation by phosphates.